Marine Aerosol Hygroscopicity and Volatility, Measured on the Chatham Rise (New Zealand)

Luke Cravigan[a], Marc Mallet[a], Zoran Ristovski[a], Petri Vaattovaara[b], Nick Talbot[c], Gustavo Olivares[c], Mike Harvey[d], Cliff Law[d].

[a]*ILAQH, Queensland University of Technology, Brisbane, 4000, Australia.*
[b]*Department of Applied Physics, University of Eastern Finland, Kuopio, FI-70211, Finland.*
[c]*National Institute of Water and Atmospheric Research, Auckland,1010, New Zealand.*
[d]*National Institute of Water and Atmospheric Research, Wellington, 6021, New Zealand.*

Abstract. The Surface Ocean Aerosol Production (SOAP) study was undertaken in February/ March 2012 in the biologically active waters of the Chatham Rise, NZ. Aerosol hygroscopicity and volatility were examined with a volatility hygroscopicity tandem differential mobility analyser. These observations confirm results from other hygroscopicity-based studies that the dominant fraction of the observed remote marine particles were non-sea salt sulfates. Further observations are required to clarify the influences of seawater composition, meteorology and analysis techniques seasonally across different ocean basins.

Keywords: Marine aerosol, hygroscopicity, volatility, ammonium sulfate.
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INTRODUCTION

This study considers the composition of Aitken and accumulation mode remote marine particles observed at the Chatham Rise (East of New Zealand; latitude 42°S-44°S, longitude 174°E-177°E). These observations were undertaken during the IGBP-SOLAS Surface Ocean Aerosol Production (SOAP) voyage in February/March 2012 on board the research vessel RV-Tangaroa (NIWA, Wellington, New Zealand). The Chatham Rise is located in the southern Pacific Ocean and is characterized by intensive summer phytoplankton blooms. These blooms lead to high organic concentration in the water and high dimethyl sulfide concentrations in the water and gas phase.

Composition of the abundant Aitken and accumulation mode remote marine aerosol has important direct and indirect climate influences [1]. Modeling indicates that the marine organic aerosol parameterization has a significant impact on the aerosol indirect forcing [2]. Despite the importance of this aerosol source there are significant uncertainties surrounding the production mechanisms, processing and resulting ultrafine marine aerosol composition.

Typically hygroscopicity measurements indicate that the remote marine aerosol is dominated by particles with a moderately high hygroscopic growth factor (HGF) (~1.6), with a small contribution from very high HGF particles (~2), and low HGF

particles (~1.3). This is consistent with an external mixture dominated by non-sea salt sulfate with sea salt aerosol (SSA) and organics and/or anthropogenic pollution [3].

The composition of sulfate particles varies depending on the ambient ammonia concentration and level of neutralization. The hygroscopic response of sulfates can provide an indication of neutralization. Sufficiently neutralized particles, such as ammonium sulfate, display prompt deliquescence from solid to aqueous as the relative humidity is increased. In the presence of particles of intermediate neutralization no deliquescence is observed [4].

SSA is produced by bubble bursting at the ocean surface and is infrequently observed. SSA is rarely a dominant contributor to the sub 100nm diameter remote marine aerosol [3]. Wind speed is thought to be a key driver of SSA concentration [5].

Dominant organic contributions to the remote marine aerosol have also been observed, especially for sub 100nm particles during periods of high biological activity [6]. These measurements display relatively minor contributions from non-sea salt sulfates across all size ranges at times of both high and low biological activity [6].

Laboratory observations of artificially generated primary marine aerosols yield internally mixed SSA/organic aerosols with Aitken and accumulation mode organic volume fractions of 7-58% using hygroscopicity methods [7,8], and up to 80% using other methods [9].

METHOD/INSTRUMENTATION

Atmospheric ultrafine Aitken and smaller accumulation mode particles (30-150nm diameter) were studied using a Volatility Hygroscopicity Tandem Differential Mobility Analyser (VH-TDMA) [10]. The VH-TDMA uses parallel Scanning Mobility Particle Sizers (SMPS) to examine particles of a pre-selected size that have been conditioned to high humidity and/or high temperature. Compositional information was obtained by exposing particles to a controlled relative humidity (20-90%) and observing the resultant hygroscopic growth. Further information is obtained from changes in the size and hygroscopic growth as particles are exposed to high temperature (25-550°C).

In addition the remote marine aerosol distribution and concentration was characterized using an SMPS (WCPC3781) and 2 condensation particle counters (CPC3007, CPC3010). Black carbon measurements were taken with an Aetholometer as a marker for ship pollution. Complementing the VH-TDMA measurements are observations from an ultra-fine organic TDMA (UFO-TDMA). This instrument examines the change in preselected particle size ($10<d<50$nm) after being exposed to ethanol vapor, providing information on an organic volume fraction (OVF) [11].

The RV-Tangaroa route was designed to maximize the time spent in waters with high biological productivity and efforts were made to minimize the influence of ship pollution on atmospheric measurements. This resulted in the examination of areas with a broad range of water biology and chemistry under a variety of meteorological conditions.

OBSERVATIONS AND DISCUSSION

H-TDMA selected observations indicate that the 30-150 nm diameter marine aerosol was dominated by particles of moderately high hygroscopicity with fractions of the total number of ambient particles at the preselected size ranging from approximately 0.6 to 1. This is consistent with high concentrations of non-sea salt sulfates. Smaller contributions from externally mixed particles with very high hygroscopicity (number fraction of up to approximately 0.3) and low hygroscopicity (number fraction of up to approximately 0.4) were also observed. The aerosol composition appears to be broadly consistent with observations from other locations using hygroscopicity methods [3].

Volatility measurements of 50 nm particles taken within (15 February) and outside of phytoplankton blooms (2 March) are shown in Fig. 1. These particles had a HGF of 1.5 and an OVF of 6-12% an indication that they are moderately hygroscopic non-sea salt sulfates. Fig. 1 indicates that the aerosol is volatilized at approximately 150°C, presenting further evidence for the dominance of non-sea salt sulfates. Measurements taken from within and outside of the phytoplankton bloom are remarkably similar, suggesting that in this case the water composition hasn't played a significant influence on Aitken mode particle composition.

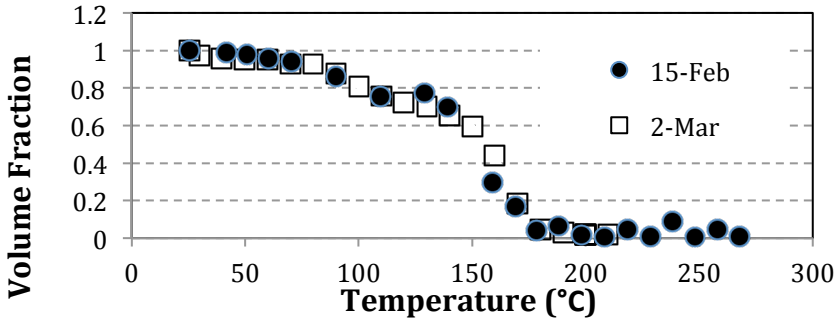

FIGURE 1. Volatility of 50 nm marine aerosol particles from within phytoplankton bloom (15 February) and outside of bloom (2 March).

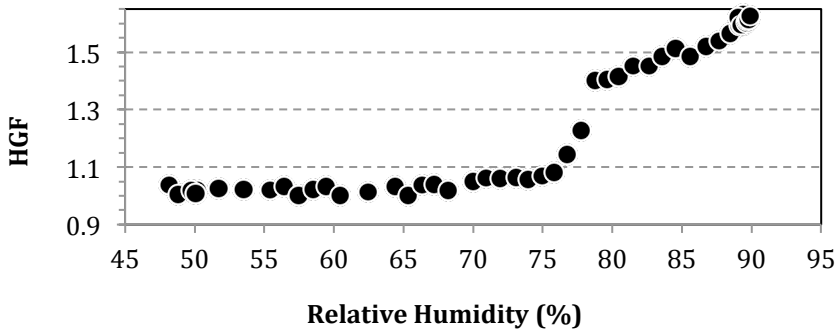

FIGURE 2. Deliquescence of 50 nm marine aerosol particles from outside of phytoplankton bloom (26 February).

Figure 2 shows the deliquescence measurements of 50 nm particles outside the phytoplankton bloom. The growth of ~1.6 observed at 90% RH is a further evidence

for the dominant presence of non-sea salt sulfates. An increase in the HGF above 1 is observed above approximately 70% RH, indicating that the dominant proportion of particles had neutralization greater than or equal to that of letovicite [4]. A reasonably prompt deliquescence can be seen between approximately 76% and 79% relative humidity, this is consistent with the deliquescence point of ammonium sulfate for 50 nm particles. The hygroscopic response suggests that the aerosol is dominated by ammonium sulfate and that ambient ammonia concentrations were high, possibly due to biogenic emissions. The UFO-TDMA also observed the dominance of ammonium sulfate on the early morning of 26th by an OVF value of 6%.

These observations confirm results from many other hygroscopicity-based studies indicating that the dominant fraction of the observed remote marine particles were non-sea salt sulfates. It appears that the composition of the secondary sulfate particles was relatively constant, indicating limited response to changes in the water biology surrounding the ship or a constant regional source. There were no atmospheric observations indicating a significant proportion of primary organics, despite measurements being undertaken in biologically active waters. Further observations are required to clarify the influences of seawater composition, meteorology and analysis techniques seasonally across different ocean basins.

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